

HYDROGEN TRANSFER REACTIONS IN COAL/TYRE LIQUEFACTION : QUANTIFICATION OF H-DONOR CONTENTS.

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Introduction

The traditional view of the mechanism of coal liquefaction of thermal cleavage followed by radical stabilisation by hydrogen transfer explained why solvents with a good hydrogen donor potential were the best solvents for coal liquefaction. The excellent work by McMillen et al ⁽¹⁾ effectively challenged this traditional view and showed that the solvent could be even more reactive and could initiate bond cleavage. The actual situation is probably a combination of the two, with the weaker linkages between polyaromatic centres undergoing thermal cleavage followed by radical stabilisation and the stronger linkages undergoing solvent initiated cleavage followed by radical stabilisation. For the weaker bonds, the rate determining step would be radical stabilisation whereas solvent initiated cleavage would be rate determining for stronger bonds.

As shown by the research of McMillen et al, certain hydroaromatic molecules are more effective than others at initiating cleavage. Bate and Harrison ⁽²⁾ emphasised this point by showing that symmetrical octahydrophenanthrene was much more effective than its antisymmetric isomer at inducing bond cleavage. Thus ideally it would be useful to have not only a measure of the total H-donor content, but also an indication of the relative amounts of individual donors. Unfortunately, the complex composition of a liquefaction process solvent (LPS) makes identification and hence quantification of individual donors difficult if not impossible even by gc-ms so that only measurements of total H-donor contents are usually carried out.

Various methods have been developed to quantify H-donor contents. Our research has made extensive use of sulphur as a H-acceptor, following an approach developed originally by Aiura et al ⁽³⁾ and modified later by Bate and Harrison ⁽⁴⁾. This method has produced results which agree well with other methods, both for model compounds and LPS's. When other materials are introduced into the liquefaction mixture, measurement of H-donor contents becomes more difficult, especially when an highly aromatic material such as tyre pyrolysis oil (TPO) is introduced. This paper examines the sulphur test approach using various substituted aromatic compounds and relates the results to measurements of H-donor contents of TPO and TPO/LPS mixtures.

Experimental

Materials

A bulk sample of TPO was provided by Bevan Recycling and a sample of hydrogenated anthracene oil (HAO) was provided by British Coal Corporation, who also supplied a sample of Point of Ayr (POA) coal and the sulphided NiMo catalyst used for hydrogenation experiments. POA coal had the following analysis : moisture 3.8, ash 14.6, volatile matter 30.9 wt% as received basis; C 68.4, H 4.7, O 8.4, N 1.34 wt% dmmf; S 2.59 wt% dry basis

Coal dissolution

Coal, TPO (or hydrogenated TPO, HTPO) and HAO were reacted in spinning/falling basket autoclaves at 400°C for 1 h. After the autoclave had cooled, the contents were removed and filtered under vacuum through glass fibre filter paper. The dichloromethane -insoluble residue was Soxhlet extracted with THF. The solid residue was dried to constant weight and its ash content was determined to calculate percentage dissolution by ash balance.

Solvent hydrogenation

Samples (150g) of TPO were hydrogenated at 420°C for various lengths of time at an initial H₂ overpressure at temperature of 170 bar, using sulphided NiMo catalyst (5g) in the spinning/falling basket autoclave. The catalyst basket was retained above the liquid charge until the temperature reached 370°C when it was released to stir in the charge at 500 rpm. After the autoclave had cooled, the liquid contents were removed by suction and stored in sealed glass jars.

H-donor tests

Weighed amounts of sulphur and test material (approximately 0.5g each giving an excess of sulphur) were introduced into a bomb type autoclave. The bomb was connected to a pressure transducer and placed in its electrical heater. The bomb was heated to its set temperature and its pressure reading noted. For the model compound test materials, the contents of the bomb were dissolved in dichloromethane and most of the excess sulphur was removed by evaporating the

dichloromethane and extracting with diethylether. The diethylether extract was analysed by gc-ms using a VG-TRIO-1 bench top quadrupole mass spectrometer with a direct capillary interface (DB17 column) from a Carlo Erba HRGC 5160 chromatograph.

Results and Discussion

Figure 1 shows a plot of relative dissolution of POA coal in various HTPO samples against the relative H-donor content of the HTPO sample. The base line represents the situation if dissolution was not being enhanced by using HTPO rather than HAO. As expected the percentage dissolution increased with increasing H-donor content, but unexpectedly dissolution was enhanced. Figure 2 shows the influence of adding various amounts of TPO or HTPO to HAO in solvent augmented coal dissolution. The H-donor content of the HTPO sample was 85% of that of HAO and the TPO sample, 23% of HAO. On addition of TPO, dissolution was reduced but not as much as might be expected by the reduction in the H-donor content alone. This point was emphasised by the increase in dissolution when HTPO was added. This apparent improvement in coal dissolution ability can be either related to compounds in the HTPO/TPO samples having a better potential to initiate bond cleavage in POA coal than the compounds in HAO, or to the sulphur procedure underestimating the H-donor content.

Analysis of TPO samples has shown that they contain a considerable content of alkyl-substituted aromatic compounds (much more than is present in HAO), and only a very low content of hydroaromatic compounds.⁽⁵⁾ Consequently the sulphur test procedure was carried out with a series of alkyl-substituted aromatic compounds to assess their influence. Table 1 shows the results relative to a base sample of hydrogenated phenanthrene (HP) at three temperatures. The TPO sample tested had been pre-distilled to remove material boiling below 275°C. Obviously a pressure increase would result from the vapour pressure of the model compound, all of which would boil below 275°C at atmospheric pressure. As an approximation, the values for toluene could be subtracted from the other values (not TPO or HP) to indicate potential of reaction with sulphur. Certain trends can be derived from the results :- (i) the number of aromatic rings - the free radicals generated by hydrogen abstraction by sulphenyl radicals will be stabilised more effectively as the number of aromatic rings increases (a fact that is important in the relative effectiveness of H-donors to initiate bond cleavage); (ii) the degree of substitution - this dependency is not as great as the previous one and probably relates to the likelihood of occurrence of cyclisation reactions; and (iii) the position of substitution - certainly 2-methylnaphthalene reacted more than 1-methylnaphthalene and para xylene did not show the same reactivity as ortho and meta xylene, probably again as a result of the likelihood of cyclisation reactions. In addition, the high reactivity of TPO should be noted.

The reactions of a wide range of hydroaromatic compounds have been reviewed.⁽⁶⁾ The reactions were initiated by abstraction of hydrogen from a benzylic position to produce a hydroarene radical. Combination of a sulphenyl radical with the hydroarene radical produced sulphur adducts which may react to release H₂S and form the dehydrogenated hydroaromatic. The review also suggested that toluene could dimerise to stilbene and 1,1'-dimethy biphenyl could cyclise to phenanthrene, each resulting in the production of H₂S. Analysis of the reaction products confirmed these earlier observation, e.g. small amounts of stilbene together with bibenzyl were identified in the toluene reaction. The gc-ms also confirmed that cyclisation reactions had occurred, producing benzothiophenes, benzodithiophenes, dithiols and phenyl thiophenes. The production of such sulphur heterocycles may have a bearing on the direct inclusion of tyre pieces into coal liquefaction. Sulphur is included in tyre formulations and breakdown of the tyre radicals could produce sulphenyl radicals which could abstract hydrogen causing retrograde reactions and depletion of valuable H-donors.

The outcome of these results is that the sulphur test would over rather than underestimate the H-donor contents. Therefore, the presence of alkyl substitution in LPS's could be advantageous. Hydropyrenes are more effective than hydrophenanthrenes at initiating bond cleavage for model compounds, reducing the activation energy for the cleavage of the ether bond in diarylethers by about 50 kJ mol⁻¹ and the alkyl link in diarylmethanes by at least 50 kJ mol⁻¹.⁽⁷⁾ However large amounts of hydropyrenes were not found in HTPO's which tended to contain more hydroderivatives of alkyl-substituted phenanthrene. Thus addition of HTPO to liquefaction, either by addition after the coal dissolution stage as TPO or by separate hydrogenation and addition at the dissolution stage could be beneficial; but the addition of tyre pieces could have both negative (production of sulphur heterocycles) and positive (improved solvent properties) effects.

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Table 1. Pressure readings per unit mass relative to hydrogenated phenanthrene (HP) for H-donor test using sulphur. n/v - no value.

Sample	Relative reading at temperature		
	230°C	275°C	300°C
toluene	0.24	0.24	0.28
ethyl benzene	0.28	0.78	0.79
o-xylene	0.26	0.32	0.46
m-xylene	0.26	0.32	0.44
p-xylene	0.26	0.29	0.29
1-methylnaphthalene	0.16	0.46	0.79
2-methylnaphthalene	0.18	0.74	0.90
dimethylnaphthalene	n/v	0.87	0.95
TPO	0.69	0.74	0.71
HP	1.0	1.0	1.0

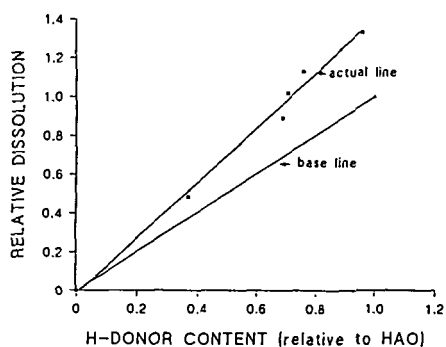


Figure 1 Graph of dissolution vs. H-donor content relative to HAO
- base line shows situation for no enhancement

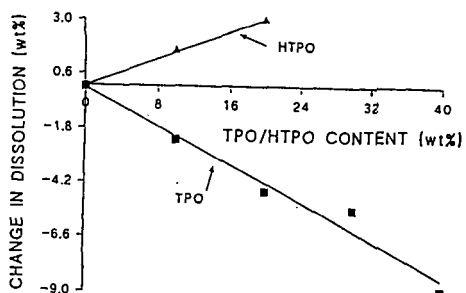


Figure 2 Graph of change in dissolution relative to HAO vs.
amount of augmenting solvent